Indian J. Phys. **79(6)**, 643-645 (2005)

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AN INTERNATIONAL JOURNAL

IJP

Comparison of microwave absorption and dielectric relaxation of some benzene derivatives and their binary mixtures

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Received 22 November 2004, accepted 23 March 2005

Abstract : The dielectric absorption of some benzene derivatives and their binary mixtures have been studied at 10.03 GHz frequency in the range of temperature of 25°C–45°C. The relaxation time, dipole moment, and the thermodynamic parameters, free energy of activation (ΔF_ε), enthalpy of activation (ΔH_ε) and entropy of activation (ΔS_ε) for relaxation process have been measured. The results have been discussed on the basis of molecular size, molecular polarity, molecular environment, molecular interaction, effect of localisation of charge density and contribution for the formation of H-bond structure.

Keywords : Dielectric relaxation, dipolemoment, activation energy, microwave absorption.

PACS Nos. : 77.22.Gm, 78.70.Gq

The benzene derivatives are important in the synthetic organic chemistry as well as a solvent system. The dielectric properties are most significant in deciding their utility. The benzene derivatives ortho-dichlorobenzene (O-$C_6H_4Cl_2$), ortho-dibromobenzene (O-$C_6H_4Br_2$), toluene ($C_6H_5CH_3$) and aniline ($C_6H_5NH_2$) are selected for study to explore the behaviour of compounds with higher as well as with lower dipole moments.

Using the method of Heston *et al* [1], the dielectric constant (ε'), dielectric loss (ε'') of the single compounds and the binary mixtures in benzene solvent at 10.03 GHz frequency at the temperatures of 25°C, 35°C and 45°C have been measured using the relations

$$\varepsilon' = \left[\frac{\lambda_0}{\lambda_d}\right]^2 + \left[\frac{\lambda_0}{\lambda_c}\right]^2 \tag{1}$$

and

$$\varepsilon'' = \left[\frac{\lambda_0^2}{\lambda_g \lambda_d}\right] \frac{\delta^1/\rho_n}{\delta n} \tag{2}$$

where λ_0 = free space wavelength, λ_c = cut off wavelength, λ_d = wavelength in the dielectric filled guide and the loss tangent tan $\delta = \varepsilon''/\varepsilon'$.

With the help of Gopalakrishna's method [2], the relaxation time (τ) and dipole moment (μ) have been measured. Debye's equation for the complex dielectric constant as a function of frequency for a dilute solution of a polar compound in a non-polar solvent can be written as

$$\frac{\varepsilon^* - 1}{\varepsilon^* + 1} = \frac{\varepsilon_\alpha - 1}{\varepsilon_\alpha + 2} + \frac{4\pi n\mu^2}{9kT} \frac{1}{1 + i\omega\tau} \tag{3}$$

where n is the number of dipole molecules per unit volume and ε^* is the complex dielectric constant of the solution, ε_α is the dielectric constant at optical range. Putting $\varepsilon^* = \varepsilon' + i\varepsilon''$ and splitting the real and imaginary parts, we obtain

$$\frac{\varepsilon' + \varepsilon' - 2}{(\varepsilon' + 2)^2 + \varepsilon''^2} = \frac{\varepsilon_\alpha - 1}{\varepsilon_\alpha + 2} \cdot \frac{4\pi n\mu^2}{9kT} \frac{}{1} \tag{4}$$

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and

$$\frac{3\varepsilon''}{(\varepsilon'+2)+\varepsilon''^2} = \frac{4\pi n\mu^2}{9kT}\frac{\omega\tau}{1+\omega^2\tau^2} = y. \quad (5)$$

At low concentration, let $(\varepsilon_\alpha - 1)/(\varepsilon_\alpha + 2) = P$

Substituting eq. [4] in [3], now we get

$$x = P + \frac{\cdot}{\omega\tau}\, y. \quad (6)$$

Hence, the slope of the graph between x and y gives the value of τ.

For estimating μ, the eq. [4] can be written as

$$x = P + \frac{4\pi Ndw\mu^2}{9kTM}$$

where M is the molecular weight, w is the weight fraction, d is the density of the liquid. The slope of the graph of x and w is equal to $4\pi Nd\mu^2/9kTM$ and from this μ can be calculated.

Using Eyring's rate process eq. [3] (ΔF_ε), (ΔH_ε) and (ΔS_ε) have been calculated by using the equations

$$\tau = \frac{h}{kT}\exp\left(\frac{\Delta F_\varepsilon}{RT}\right),$$

and $\Delta F_\varepsilon = \Delta H_\varepsilon - T\Delta S_\varepsilon$.

The dielectric constant (ε'), dielectric loss (ε'') of the samples in dilute benzene solution at 10.03 GHz have been measured by using an X-band microwave bench. The microwave generated by a Gunn oscillator is passed through the wave guide set to the liquid cell having provision for hotwater circulation arrangement for the control of temperature.

The values of τ, μ and the thermodynamical parameters ΔF_ε, ΔH_ε and ΔS_ε of the single compound and the binary mixtures have been presented in Tables 1 and 2, respectively.

It has been observed that for both single compounds and the binary mixtures, the values of τ decrease with the increase of temperature [4–7]. With the increase of temperature, the loss of energy increases due to increase of molecular collisions with temperature. The relaxation time of dibromobenzene is largest and that of aniline is smallest among all the single compounds. This is because the bromine group of dibromobenzene polarizes the solvent molecules more strongly as compared to the others. The smaller values of (τ) for aniline which agree with the values of previous workers [8] is due to non-interaction of aniline with benzene molecules as strongly as the other molecules of the compounds. The values of (τ) of the binary mixture of toluene are nearly same with the single compound at the same temperature. This suggests that there is no solute-solute or solute solvent type of interaction of toluene in the mixture.

For both the single compounds and the binary mixtures, the (μ) values increase with temperature. This is due to the gain of K.E. of the molecules resulting the decrease in steric hindrance for the free rotation of the molecules. The largest values of (μ) for dichlorobenzene is due to more charge localisation as the substituent chlorine has more electronegativity than the others [9].

Table 1. Relaxation time (τ), dipole moment (μ), free energy of activation (ΔF_ε), enthalpy of activation (ΔH_ε) and entropy of activation (ΔS_ε) of the single compounds.

Sample	Temp. °C	τ ps	μ Debye	ΔF_ε K-Cal/ mole	ΔH_ε K-Cal/ mole	ΔS_ε Cal/ mole K
Ortho-	25	7	1.26	2.23		−1.34
dicholorobenzene	35	6.4	1.30	2.26	1.84	−1.36
	45	5.7	1.37	2.28		−1.38
Ortho-	25	10.3	1.06	2.45		−2.11
dibromobenzene	35	9.2	1.10	2.48	1.82	−2.14
	45	7.96	1.15	2.50		−2.10
Toluene	25	6.8	0.42	2.17		3.45
	35	6.3	0.67	2.23	3.2	3.18
	45	5.3	0.70	2.24		3.02
Aniline	25	2.3	1.02	1.50		4.6
	35	2	1.04	1.54	2.9	4.4
	45	1.8	1.09	1.57		4.2

As the electro-negativity of carbon is low, the localisation of charge of toluene is less, resulting the low value of μ. For the binary mixture of dichlorobenzene, dibromobenzene and aniline, the μ is greater than that of the individual compounds. This may be due to the contribution for the hydrogen bonded structure occurring in the binary mixtures. The small value of μ for the binary mixture of toluene shows that in the presence of toluene, the charge localisation is less which is largely due to less electron density in toluene as well as low electro-negativity of carbon. Due to individual low value of μ and less hydrogen bonding compared to other mixtures, the value of μ for the mixture of toluene and aniline is smaller.

The values of ΔS_ε for dichlorobenzene and dibromobenzene are negative while for toluene and aniline are positive. This suggests that for dichlorobenzene and dibromobenzene, most probable configurations involve in

Table 2. Relaxation time (τ), dipole moment (μ), free energy of activation (ΔF_ε), enthalpy of activation (ΔH_ε) and entropy of activation (ΔS_ε) of the binary mixtures.

Sample	Temp. °C	τ ps	μ Debye	ΔF_ε K-Cal/ mole	ΔH_ε K-Cal/ mole	ΔS_ε Cal/ mole K
Dichlorobenzene	25	9.5	1.27	2.37		−1.84
+	35	7.7	1.33	2.38	1.85	−1.72
Dibromobenzene	45	6.6	1.39	2.4		−1.63
Dichlorobenzene	25	6.7	0.91	2.19		2.98
+	35	6.2	0.92	2.41	3.32	2.95
Toluene	45	5.6	0.928	2.45		2.89
Dichlorobenzene	25	4.8	1.37	2.01		5.03
+	35	3.7	1.42	2.10	3.5	4.54
Aniline	45	2.9	1.52	2.24		3.96
Dibromobenzene	25	9.76	0.73	2.42		2.60
+	35	8.1	0.96	2.58	3.2	2.10
Toluene	45	7.5	0.98	2.63		1.79
Dibromobenzene	25	5.5	1.05	2.081		5.09
+	35	4.7	1.50	2.175	3.6	4.62
Aniline	45	3.5	1.65	2.246		3.59
Toluene	25	6.4	0.90	2.17		5.8
+	35	5.1	1.05	2.29	3.9	5.2
Aniline	45	4.5	1.1	2.31		5.0

dipole orientation and the activated state is of more ordered than the normal state, but for toluene and aniline, the environment for the system is not cooperative for the system and the activated system less ordered than the normal state. The values of ΔS_ε for the binary mixture of dichlorobenzene and dibromobenzene are negative. This suggests the cooperative orientation for dipole-dipole interaction of the molecules in the binary mixture. The values of (ΔS_ε) for the binary mixture of toluene and aniline with each of the compounds are positive. This suggests that the environment for the system is not cooperative and the activated system is less ordered than the normal state.

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